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(54) HIGH TEMPERATURE RESISTANT THERMAL SPRAY-COATING MEMBER

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a dense composite thermal spray-coating film tight in adhesion by forming an alloy thermal spray-coating film obtd. by thermally spraying in an evacuated atmosphere contg. no oxygen on the surface of a metallic base material and forming an Al thermal spray-coating film obtd. by thermal- spraying Al or an Al alloy in the same atmosphere thereon.

SOLUTION: The composition of alloy thermal spray-coating film as an under coat is shown as MCrAlX, where M is one or more kinds among Ni, Co and Fe and X is one or more kinds among Y, Hf, Ta, Cs, Ce, La, Th, W, Si, Pt and Yb. The composite coating film composed of the MCrAlX alloy coating film and Al or Al alloy coating film as an over coat can be used as it is, but it is suitable that heat treatment is executed at 900 to 1200°C for 0.5 to 10 hr in the air, in an inert gas or in a vacuum. In this way, metallurgical bonding between the MCrAlX alloy grains to each other and between those and the Al or Al alloy grains is increased to improve its denseness and also to exhibit its high temp. oxidation resistance.

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CLAIMS

[Claim(s)]

[Claim 1] The MCrAlX alloy obtained by carrying out thermal spraying as a under coat on the surface of a metal base in the reduced pressure atmosphere which does not contain oxygen (however, M -- one sort of nickel, Co, and Fe or two sorts or more, and X -- one sort of Y, Hf, Ta, Cs, Ce, La, Th, W, Si, Pt, and Yb, or two sorts or more) A sprayed coating is formed. elevated-temperature-proof flame spraying characterized by forming aluminum sprayed coating obtained by carrying out thermal spraying of aluminum or the aluminum alloy in the same atmosphere as an overcoat on it -- a member

[Claim 2] The MCrAlX alloy obtained by carrying out thermal spraying as a under coat on the surface of a metal base in the reduced pressure atmosphere which does not contain oxygen (however, M -- one sort of nickel, Co, and Fe or two sorts or more, and X -- one sort of Y, Hf, Ta, Cs, Ce, La, Th, W, Si, Pt, and Yb, or two sorts or more) A sprayed coating is formed. aluminum or aluminum alloy sprayed coating obtained by carrying out thermal spraying in the same atmosphere as an overcoat on it is formed. and the sprayed coating -- inside of the atmosphere, nonoxidizing atmosphere, or a vacuum 900-1200 degrees C and 0.5 elevated-temperature-proof flame spraying characterized by having the heatproof and anti-oxidation layer obtained by performing heat treatment of time - 5 hours -- member

[Claim 3] elevated-temperature-proof flame spraying according to claim 1 or 2 characterized by forming further the oxide system ceramic sprayed coating obtained by carrying out the plasma metal spray in the atmosphere as topcoat on the above-mentioned sprayed coating formed as an overcoat -- a member

[Claim 4] elevated-temperature-proof flame spraying given in any 1 term of the claims 1-3 characterized by containing 2 - 18wt% aluminum intermetallic compound as an aluminum content in the above-mentioned MCrAlX alloy sprayed coating formed as a under coat -- a member

[Claim 5] elevated-temperature-proof flame spraying given in any 1 term of one to claim 4 term characterized by forming a under coat, an overcoat, and/or topcoat over two or more layers -- a member

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[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] this invention relates to the flame-spraying member suitably used as members for the elevated-temperature contamination sections, such as a boiler, a gas turbine, a jet engine, and a diesel power plant. The flame-spraying member of this invention offers what is used as a heat-resistant member in fields, such as a shaft furnace, a heat treating furnace, a rocket, a space shuttle, and a gas engine.
[0002]
[Description of the Prior Art] It is well known that energetic development research is advanced for the purpose of improvement in thermal efficiency in prime-mover Seki, such as a diesel, a boiler, a gas turbine, and a jet engine. However, the improvement in thermal efficiency has also brought simultaneously a result which forces it the increase of a severe thermal load to a composition member. Therefore, while having a high mechanical strength under an operating environment as a metallic material used for the elevated-temperature section of these prime-mover Seki, to excel in high-temperature-oxidation-proof nature and high-temperature-corrosion-proof nature is demanded. since these impurity elements carry out the corrosion consumption of the metallic material violently in the state of an elevated temperature in using the fuel which contains impurities, such as V, Na, and S, especially -- ** -- it is required to maintain the state where it was stabilized also in environment [like] for a long time
[0003] In order to meet such a demand, many heat-resistant alloys which make a principal component nonferrous metal elements, such as Cr, nickel, Mo, Co, W, Ta, aluminum, and Ti, from the former and which are called so-called superalloy have been developed. However, as for addition of the metallic element by which these superalloies are not useful to improvement in intensity since a high temperature strength is given top priority, the rate tends to be suppressed low inevitably. Although the representation of the metallic element which is not useful to improvement in such intensity is Cr, aluminum, Si, etc., since these elements are excellent in oxidation resistance and high-temperature-corrosion-proof nature with one side, the superalloy which gave priority to the above high temperature strengths has scarce common one to oxidation resistance or high-temperature-corrosion-proof nature.
[0004] Under such a background, to the superalloy member used under hot environments, a metal or alloys, such as Cr, and aluminum, Si, were beforehand covered with the spraying process, the diffusion penetration method, etc. on the front face, and the fall of a resistance force to the chemical injury on a superalloy is compensated. However, at a spraying process, the coat which processed the advantage which can choose the kind of thermal spray material arbitrarily in the atmosphere of a certain thing has the fault of being scarce in corrosion resistance and adhesion by porosity. although the fault which the method (low-pressure-plasma-spraying method) of performing a plasma metal spray in this point and a low-pressure argon gas atmosphere which does not contain air (oxygen) substantially in recent years is developed, and an air sprayed coating has has improved sharply -- the bottom of the elevated-temperature contamination environmental condition of these days -- ** -- a coat [like] -- already -- enough -- **** -- it is impossible to say Moreover, it is hard to say that oxidation resistance and high-temperature-corrosion-proof nature are enough, and although the conventional diffusion penetration method is comparatively easy when processing Cr, aluminum, Si, etc. independently, respectively, since it is necessary to process in the state of the elevated temperature around 1000 degrees C, by this approach, there is a fault that the mechanical property of a superalloy base material deteriorates.
[0005] After carrying out thermal spraying of the nickel-Cr alloy which is an oxidation resistant metal by JP,55-104471,A to such a situation, the method of performing pack cementation, such as aluminum and Cr, is proposed. However, although there is an outstanding thing in improvement in the adhesion of a sprayed coating, or compactness, since, as for this method, the processing peculiar to a diffusion penetration method under an elevated temperature is not avoided, deterioration of the mechanical property of a base material has too the problem that it cannot escape.
[0006] On the other hand, development of the thermal spray material itself used under this kind of hot environments is also performed actively. The typical thing is the heat-resistant alloy shown by MCrAlX (here, M is nickel, Co, Fe(s), or

two or more of these carat groups, and X is the element of Y, Hf, Ta, Cs, Pt, Ce, Zr, La, Si, Th, etc.). formation of the coat which is rich in very advanced oxidation resistance and high-temperature-corrosion-proof nature by carrying out low pressure plasma spraying of this MCrAlX alloy is possible -- becoming -- an elevated temperature -- the performance of a member improved much more

[0007] Furthermore, after forming this kind of MCrAlX alloy sprayed coating, the method of performing pack cementation, such as Cr and aluminum, further is also proposed (for example, JP,61-10034,B). However, however it could not say that the gas turbine member by which today was elevated-temperature-ized was enough as the endurance and might use the excellent sprayed coating also with such newest spraying process and the combination of a spraying process and pack cementation, as long as it combined with pack cementation, it had left the problem at the place which deterioration of the mechanical property of a base material cannot escape.

[0008] development of the technology which combined such a spraying process, newest spraying process, and newest pack cementation -- a gas turbine -- the life of a member has improved considerably However, it also inquires still more energetically about the gas turbine itself now, and it is expected that the highest use gas temperature of a gas turbine will amount to no less than 1500-1700 degrees C in the future. Though the gas turbine member in contact with such elevated-temperature gas strengthens the cooler style by air or the steam, the contamination temperature of a member is present. It exceeds 900 degrees C and a bird clapper is expected by about 950-1050 degrees C. for this reason, present and a gas turbine -- improvement in the high temperature strength of the metal base of a member itself is going to be aimed at

[0009]

[Problem(s) to be Solved by the Invention] Now, the technical problem which it is going to solve by this invention is as follows.

(1) All of the MCrAlX alloy of the various composition marketed are alloyed, and the melting point is very high. (before or after 1400 degrees C) It is general. For this reason, though thermal spraying of the inside of the atmosphere is carried out in Ar gas under the reduced pressure which does not contain oxygen substantially from the first, it involves in gas in the state of thermal spraying, and pore generates it in a coat. Then, while heating this coat at 1000-1100 degrees C in a vacuum, combining mutually the spray particle which constitutes a coat and reducing porosity, usually improvement in the adhesion of a coat is aimed at by making it spread also into a parent metal. thus -- even if it carries out low pressure plasma spraying of the MCrAlX alloy -- in addition -- and since hot heat treatment is needed, the deterioration of the mechanical property of a parent metal and the increase of cost accompanying this are a big problem

[0010] However, the above-mentioned MCrAlX alloy currently used under the conventional technology grinds, after alloying in a vacuum melting furnace, and it is taken as the spray particle. Therefore, all the metallic elements that constitute an alloy are alloyed by the metallurgical reaction, and though low aluminum (660 **)- of the melting point, however - which this aluminum dissolved completely and has turned into Alloying aluminum are included, the melting point as the whole alloy has become 1400-degree-C order. For this reason, even if it heats a MCrAlX alloy in the low-pressure-plasma-spraying back and temperature of about 900-1000 degrees C, the cross coupling reaction of the MCrAlX alloy particle which constitutes a coat, and the junction reaction with a base material alloy are slow, and inadequate. so, heat treatment in the elevated temperature around 1100 degrees C is indispensable in a vacuum, and obliged [with the consumption which is great energy and an effort] to deterioration of the mechanical property of a base material alloy about the conventional technology

[0011] On the other hand, for the high-temperature-oxidation-proof nature of these MCrAlX alloys, aluminum and Cr which are contained in the alloy when exposed to hot environments are aluminum 2O3 and Cr 2O3, respectively. Although generated by becoming an oxide and covering an outside surface, it is Cr 2O3. At the elevated temperature of 1000 degrees C or more, it is set to CrO3 with high vapor pressure, and vaporizes. Therefore, under such a high temperature service, it is stable aluminum 2O3 chemically rather. The direction of oxidation resistance is good. The aluminum 2O3 aluminum for generating is a MCrAlX alloy. (aluminum:1 - 29wt% is contained) Since it is contained in inside so much, if it sees from the point of high-temperature-oxidation-proof nature, it will be thought that it is in the state of being mostly satisfied. however, since aluminum system intermetallic compound is included so much, the sprayed coating which formed aluminum using the included MCrAlX alloy is firmly weak, and they are few at an operating environment -- it is mechanical When a thermal shock was got, there was a trouble destroyed easily.

[0012] Moreover, generally the conventional technology which the outside surface of the MCrAlX alloy sprayed coating which is a under coat is made to carry out diffusion osmosis of aluminum or the Cr, and gives high-temperature-oxidation-proof nature to it is the following processes.;

** after MCrAlX alloy thermal spraying, Cr, aluminum pack cementation (900-1100 degrees C, 5 -10h heating), and ** -- subsequently -- base material (nickel machine alloy) Solution treatment (1050-1150 degrees C, 1-8h) They are the aging treatment (750-900 **, 1-10h) of a base material, and the thing come out of and processed after that [**].

Moreover, this is often heat-treated after MCrAlX alloy thermal spraying (900-1200 degrees C, 2-20h), and Cr and carrying out aluminum pack cementation are also adopted in this coat. Cr, since aluminum pack cementation is carried out, although it is made to spread, and the compactness and adhesion of the sprayed coating itself improve a sprayed coating in the case of such technology -- after that In order to heat at 900-1100 degrees C, the mechanical strength of a base material falls, therefore heat treatment of ** of upper ** and ** is needed, and excessive energy and an excessive effort must be used.

[0013] In order to solve the problem of the various kinds mentioned above which the conventional MCrAlX alloy sprayed coating has, one of artificers is JP,6-306567,A and a publication number previously. It is aluminum 2O3 to the outside surface of sprayed-coating-izing which consists of a MCrAlX alloy which is indicated by 6 No. -322507 official report, and a metal aluminum of a free state. The technology which builds a MCrAlX alloy coat with high concentration was proposed. however, aluminum 2O3 which concentration was higher, was precise and was excellent in high-temperature-oxidation-proof nature when it was contaminated in hot combustion gas, while heightening the cross coupling force of the MCrAlX alloy particle which constitutes a sprayed coating further, although the desired end was attained about this technology It is the point of the operation to form, in addition there was room of an improvement.

[0014] Then, the purpose of this invention is precise and is to offer the high-temperature-service-proof member covered with the composite-spraying coat with sufficient adhesion. Other purposes of this invention have the mechanical strength of a base material in offering a high elevated-temperature-proof flame-spraying member. The purpose of further others of this invention is cheap, and is to offer the easy elevated-temperature-proof flame-spraying member of manufacture.

[0015]

[Means for Solving the Problem] As a result of repeating research wholeheartedly, in order to attain the desired end that artificers should improve point ****** which solved the aforementioned problem and one of artificers proposed previously After forming membranes by carrying out thermal spraying of the MCrAlX alloy under reduced pressure argon atmosphere, in the same reduced pressure argon atmosphere Plasma Electric arc The knowledge that it was effective that carry out thermal spraying of aluminum or the aluminum alloy, and it carries out a laminating by the spraying process which makes electrical energy of laser etc. a heat source was acquired.

[0016] this invention completed under such knowledge on the surface of a metal base as a under coat The MCrAlX alloy obtained by carrying out thermal spraying in the reduced pressure atmosphere which does not contain oxygen (however, M -- one sort of nickel, Co, and Fe or two sorts or more, and X -- one sort of Y, Hf, Ta, Cs, Ce, La, Th, W, Si, Pt, and Yb, or two sorts or more) A sprayed coating is formed. elevated-temperature-proof flame spraying characterized by forming aluminum sprayed coating obtained by carrying out thermal spraying of aluminum or the aluminum alloy in the same atmosphere as an overcoat on it -- it is a member

[0017] The MCrAlX alloy obtained by carrying out thermal spraying of this invention as a under coat on the surface of a metal base in the reduced pressure atmosphere which does not contain oxygen again (however, M -- one sort of nickel, Co, and Fe or two sorts or more, and X -- one sort of Y, Hf, Ta, Cs, Ce, La, tH, W, Si, Pt, and Yb, or two sorts or more) A sprayed coating is formed. aluminum or aluminum alloy sprayed coating obtained by carrying out thermal spraying in the same atmosphere as an overcoat on it is formed. And it is in the atmosphere, nonoxidizing atmosphere, or a vacuum about the sprayed coating. 900-1200 degrees C and 0.5 The elevated-temperature-proof flame-spraying member characterized by having the heatproof and anti-oxidation layer obtained by performing heat treatment of time - 5 hours is proposed.

[0018] In addition, in this invention, it is desirable that the oxide system ceramic sprayed coating obtained by carrying out the plasma metal spray in the atmosphere as topcoat is further formed on the above-mentioned sprayed coating formed as an overcoat. Moreover, in this invention, it is desirable to contain 2 - 18wt% aluminum intermetallic compound as an aluminum content in the above-mentioned MCrAlX alloy sprayed coating formed as a under coat. Moreover, in this invention, it is desirable that a under coat, an overcoat, and/or topcoat are formed over two or more layers.

[0019]

[Embodiments of the Invention] this invention is mainly a MCrAlX alloy sprayed coating. (under coat) aluminum or aluminum alloy sprayed coating (topcoat) And it consists of oxide system ceramic sprayed coatings if needed. The mechanism of action of the sprayed coating formed by this invention is explained first below.

[0020] There is a property as shown below in the MCrAlX alloy used by this invention. That is, since the above-mentioned MCrAlX alloy consists of metallic elements with a strong chemical affinity with oxygen, it is common to use a vacuum melting furnace for alloying this. The MCrAlX alloy dissolved by this vacuum melting furnace causes a metallurgical reaction mutually in a melting state, and is many alloy metallurgy intergeneric compounds. (for example, NiAl, nickel3aluminum, Co3Ti, and Ti3aluminum, FeAl, TiAl3) Though this is ground even if and it is made thermal-

spraying powder from building, the physicochemical quality shows the property as an alloy metallurgy intergeneric compound. For this reason, though the low aluminum component of the melting point is contained in the MCrAlX alloy, the melting point is the melting point as an alloy. (before or after 1400 degrees C) It is shown. Therefore, since it is necessary to heat to the temperature around at least 1100 degrees C, after carrying out thermal spraying of this alloy, when making a sprayed coating precise by heat-treatment, degradation of a base material is caused, and also the actual condition is that still more sufficient particle degree of coupling is not obtained by this heat-treatment, either.
[0021] it is very weak and small, when this is made into a sprayed coating on the other hand, although the aforementioned aluminum intermetallic compound has the outstanding high temperature strength -- it is thermal Even if it receives a mechanical shock, there is a fault which exfoliates from a base-material front face easily. For this reason, the problem that a lot of aluminum cannot be blended is in a MCrAlX alloy.
[0022] Then, in this invention, by forming a under coat by the plasma metal spray method in the argon gas atmosphere under the reduced pressure which does not contain air for a MCrAlX alloy substantially, carrying out thermal spraying of Metal aluminum or the aluminum alloy in the reduced pressure atmosphere where it is the same on it, after that, forming an overcoat and carrying out the laminating of these, the outside surface of a sprayed coating is changed into the high state of aluminum content, and high-temperature-oxidation-proof nature was given. That is, this invention stops the amount of aluminum intermetallic compound in a under coat, and is based on the view of compensating the insufficiency with the law of an overcoat.
[0023] Since the metal aluminum used for an overcoat or aluminum alloy has strong chemical bond nature with oxygen, if thermal spraying is carried out in the atmosphere, in order to oxidize soon, aluminum or aluminum alloy thermal-spraying layer has the fault to which it becomes the aggregate of aluminum covered with the oxide, or aluminum alloy particle, and these cross coupling force becomes weak.
[0024] However, if thermal spraying of the sprayed coating is carried out in low-pressure Ar gas atmosphere, while it adheres on the MCrAlX alloy sprayed coating which is a under coat, and the alloy in the under coat will cause a metallurgical reaction, will generate heat further and diffusing aluminum or aluminum alloy particle inside a coat, without oxidizing, aluminum concentration will form a high intermetallic compound with the strong bonding strength between particles.
[0025] furthermore, the method of this invention -- carrying out -- hitting -- aluminum content in the MCrAlX alloy as a under coat -- low -- stopping -- (2 - 18wt%) While giving ductility to the sprayed coating in the direction of a under coat, the high-temperature-oxidation-proof nature which runs short for the reason aluminum thermal-spraying layer formed as an overcoat (aluminum>=98.0wt%) or aluminum alloy layer beyond aluminum+Si=95wt% -- setting -- precise -- aluminum 2O3 with sufficient adhesion You are going to make it generate.
[0026] Drawing 1 (a) and (b) The cross-section structure of the high-temperature-service-proof thermal-spraying enveloping layer of this invention is shown. Here, it is 1. The base material for processed, and 2 The MCrAlX alloy sprayed coating and 3 which were formed as a under coat It is aluminum or aluminum alloy thermal-spraying layer formed as an overcoat. Drawing 1 (a) The flame-spraying member of the two-layer structure where aluminum or aluminum alloy thermal-spraying layer which is an overcoat was made to form on the under coat which is a MCrAlX alloy sprayed coating is shown. drawing 1 (b) Drawing 1 (a) flame spraying at the time of having repeated two-layer structure twice and making it multilayer structure -- it is the example of a member In addition, although after the above-mentioned sprayed coating formation can be used also in the state as it is in this invention, it is in the atmosphere, inert gas, or a vacuum. It is more suitable to heat-treat 900-1200 degree-Cx 0.5-10Hr. While raising combination in metallurgy as the cross coupling force and the MCrAlX alloy particle and aluminum, or aluminum alloy spray particle between the MCrAlX alloy particles which constitute a sprayed coating and raising compactness with this heat treatment, it is aluminum 2O3 to an early stage in the front face of a laminating sprayed coating. It can be made to be able to generate and the high-temperature-oxidation-proof nature which was excellent from the early stages of use can be demonstrated.
[0027] Moreover, high-concentration aluminum 2O3 generated on the laminating sprayed coating front face Since this ceramic sprayed coating demonstrates good adhesion even when forming an oxide system ceramic sprayed coating, this acts effectively also as a thermal-shield coat. Drawing 1 (c) It is what showed the coat cross-section structure in other examples concerning this invention, and 4 is a ceramic sprayed coating.
[0028] The chemical composition of the MCrAlX alloy thermal spray material used for this invention is as being shown below.
M component: nickel (<=75wt%), Co (<=70wt%), Fe Cr (<=70wt%) component: (5 - 15wt%) aluminum component: (2 - 18wt%) X component : [Y (0 - 5 wt%),] Hf (0 - 10wt%), Ta (1 - 20wt%), and Cs (0 - 0.1 wt%), Ce (0 - 0.25wt%), La (0 - 10wt%), and Th (0 - 3 wt%), W (0 - 5.5 wt%), Si (0 - 20wt%), and Pt (0 - 3 wt%) -- the purity of aluminum constructed on a MCrAlX alloy under coat again -- commercial aluminum (three sorts of 99% or more of JIS H 2102) it is -- if -- it is usable

[0029] The thickness of the under coat which is a MCrAlX alloy sprayed coating is 30-500. aluminum of mum and topcoat or aluminum alloy thermal-spraying layer thickness is 5-100. mum It is desirable to control and carry out thermal spraying to within the limits. For the reason, the thickness of a under coat is 30 micrometers. When thin, a high-temperature-oxidation-proof nature life is short, and on the other hand, it is 500. mum It is because it is economically disadvantageous since there is no exceptional change in a performance even if it constructs in the above thickness. Moreover, about the thickness of aluminum formed as topcoat, or aluminum alloy sprayed coating, it is 5 micrometers. Below, thermal-spraying construction becomes unequal [thickness], and becomes unstable [a performance] a difficult top, and, on the other hand, it is 100. mum In being thick, there is a possibility of exfoliating while in use by generation of brittle aluminum rich layer.
[0030] It is plasma, in order to manufacture the elevated-temperature-proof covering member of this invention, as explained above. Electric arc The spraying process which makes electrical energy of laser etc. a heat source is used, and it is air substantially. (oxygen) It is desirable to construct in the environment which is not included, for example, inert gas, and the reduced pressure atmosphere of argon gas.
[0031] When, forming further the oxide system ceramic sprayed coating which has thermal resistance as topcoat in the maximum surface section on aluminum formed as an overcoat, or aluminum alloy sprayed coating on the other hand, it is 50-500. mum ** is suitable. For the reason, the thickness of this coat is 50 micrometers. Below, it is heat.
[0032]
[Example] an example 1 -- aluminum content as an intermetallic compound in the MCrAlX alloy constructed as a under coat in this example, and high concentration aluminum composition layer of the maximum surface section in aluminum sprayed coating formed as an overcoat on this sprayed coating (aluminum sprayed coating) It investigated about thermal and mechanical stability. That is, if the amount of aluminum contained in the MCrAlX alloy in a under coat increases, since the content of an aluminum-Co system and a aluminum-nickel system intermetallic compound will increase inevitably, although high-temperature-oxidation-proof nature improves, by becoming very weak, and heating and cooling being repeated by the coat, or a crack's occurring, if a mechanical shock is added, or exfoliating locally, the life of a coat is short and a bird clapper is expected.
[0033] then, the MCrAlX alloy which aluminum content changed in 2 - 29wt% in this example -- using -- SUS 304 Steel (size: -- width-of-face 50x length 100 x -- thick -- 6mm) one side -- a low-pressure-plasma-spraying method -- therefore -- 200 mum ** -- forming membranes -- the still more nearly same spraying process on it -- Metal aluminum -- 30 micrometers The sprayed coating test piece constructed to ** was manufactured. Thus, after holding for 15 minutes in the electric furnace which heated the manufactured test piece at 1000 degrees C, the spalling test which repeats the operation supplied to underwater [25-degree C] 10 times was performed. Moreover, as a mechanical shock, it is the particle size of 45**10 micrometers. aluminum 2O3 It is a particle 5 kgf/cm2 It has the compressed air. As opposed to the sprayed coating left 500mm 300g It evaluated using the method of injecting. [(Blast impact test) 0034] Table 1 summarizes these results. As shown in Table 1, less than [18wt%], aluminum content in the MCrAlX alloy for under coats was comparatively often equal also to the thermal shock and the blast impact test, and it turns out that ablation and consumption of topcoat are few. On the other hand, even if aluminum content in a MCrAlX alloy constructed aluminum in the maximum surface section about the under coat beyond 20wt%, a detailed crack and minute coat ablation occurred by the spalling test, and in the blast impact test, the faulted condition of these coats was accepted still more clearly. From the above result, that to suppress less than [18wt%] is required made clear aluminum content in the MCrAlX alloy set as the object of this invention.
[0035]
[Table 1]

No.	アンダーコート	オーバーコート	試験結果		備考
	MCrAlX合金溶射皮膜中のAl	Al溶射皮膜層の厚さ	熱衝撃試験	ブラスト衝撃試験	
1	2	30	異常認めず	重量減少20mg以下	発明例
2	8	30	異常認めず	同　上	
3	12	30	異常認めず	同　上	
4	14	30	異常認めず	同　上	
5	18	30	異常認めず	同　上	
6	20	30	微小剥離発生	重量減少35mg 微小割れ発生大	比較例
7	25	30	剥離大	重量減少40mg 微小割れ発生大	
8	29	30	剥離大	重量減少80mg 微小剥離発生	

(備考) (1) アンダーコート欄の数字はwt%を示す。
(2) オーバーコート欄の数字はμm を示す。
(3) アンダーコートのMCrAlX合金の基本組成は32wt%Ni-38.5 wt%Co-21 wt%Cr-8wt%Al-0.5wt%Y で、Al含有量の増減に対してはCo含有量を増減することによって調整した。
(4) 熱衝撃試験条件　1000℃×15min →25℃水中投入10回繰返し
(5) ブラスト衝撃試験条件　Al_2O_3 粒子を5 kgf/cm² の圧縮空気を用いて 500mmの距離から300gを噴射。

[0036] an example 2 -- in this example, the MCrAlX alloy thermal spray material which has component composition as shown in Table 2 was used Namely, the MCrAlX alloy with which A does not contain nickel, the MCrAlX alloy with which B does not contain Co, the MCrAlX alloy with which C contains nickel and Co, and D contain nickel and Co, and are Y as an X component further. It is a MCrAlX alloy containing Ta.
[0037] A sprayed coating test piece four kinds of MCrAlX alloys shown in Table 2 by the low-pressure-plasma-spraying method nickel machine alloy base material (8.2 wt%Cr-10wt%Co-10wt%W-3wt%Ta-5.5wt%aluminum-1.5 wt%Hf-1.0wt%Ti-** wt%nickel) It is 300 upwards. mum After forming membranes to **, It is 50 micrometers about Metal aluminum in the still more nearly same atmosphere. It constructed to **. The cross-section structure of these sprayed coatings is the same as that of what was previously shown in drawing 1 (a). What performed heat treatment of 1080 degree-Cx1h in the vacuum furnace for a part of obtained MCrAlX alloy sprayed coating here, and coat with thermal spraying (coat which does not heat-treat) About two kinds, the porosity of a coat was measured [cross section / coat / each] using image-analysis equipment.
[0038] Table 3 summarizes this result. Namely, aluminum sprayed coating (overcoat) MCrAlX alloy sprayed coating which does not cover and moreover does not heat-treat (No.5) With a thermal-spraying state It is porosity by performing heat treatment of 1080 degree-Cx1h for this, although the porosity of 0.5 - 1.3 % is shown. It is falling to 0.3 - 0.5 %. on the other hand, thing which has aluminum sprayed coating into a surface portion (No.1-4) Even if it does not heat-treat if it heat-treats by showing the low porosity about 0.3 - 0.4 % -- further -- It fell to 0.1 - 0.2 %. It is imagined that the porosity of a coat falls aluminum sprayed coating much more by formation SU ******, the invasion to the interior of a coat of a combustion gas component or air is prevented to the outside surface of a MCrAlX alloy sprayed coating, and the high-temperature-oxidation-proof nature of a sprayed coating may be raised to it so that clearly from this result.
[0039] In addition, like this invention, when aluminum sprayed coating is formed as an overcoat on a under coat, it is the MCrAlX alloy sprayed coating [directly under] of it. (under coat) Although the inclination for porosity to decrease a little is accepted, this is considered to be the result by which precise-ization of a MCrAlX alloy sprayed coating was promoted under the influence of the metallurgical reaction accompanied by aluminum of a heating melting state, and generation of heat of a MCrAlX alloy.
[0040]

[Table 2]

記号	化学成分 (wt%)					
	Ni	Co	Cr	Al	Y	Ta
A	—	残り	23	13	0.5	—
B	残り	—	16	6	0.8	—
C	32	残り	21	8	0.5	—
D	10	残り	25	7	0.6	5

[0041]
[Table 3]

No.	皮膜の構成		皮膜の気孔率 (%)		備考
	MCrAlX合金溶射皮膜	オーバーコートAl溶射皮膜の有無	溶射状態のまま	1080℃×1h熱処理	
1	A	有	0.3 ～ 0.4	0.1 ～ 0.15	発明例
2	B	有	0.3 ～ 0.5	0.1 ～ 0.2	
3	C	有	0.3 ～ 0.4	0.1 ～ 0.2	
4	D	有	0.3 ～ 0.4	0.1 ～ 0.15	
5	A	無	0.5 ～ 1.3	0.3 ～ 0.5	比較例
6	B	無	0.6 ～ 1.2	0.4 ～ 0.7	
7	C	無	0.6 ～ 1.0	0.3 ～ 0.5	
8	D	無	0.5 ～ 1.2	0.4 ～ 0.7	

(備考) (1) MCrAlX合金の化学組成は表2に示した。
(2) オーバーコートとしてのAl層の厚さは50μm 厚
(3) 適合例の皮膜気孔率は、オーバーコートの気孔率を示す。
(4) 比較例の気孔率は、MCrAlX合金皮膜の気孔率を示す。

[0042] an example 3 -- in this example, the elevated-temperature corrosion resistance of the member which has aluminum or aluminum alloy sprayed coating as an overcoat, and has a MCrAlX alloy sprayed coating as a under coat was investigated Co basis alloy (29wt%Cr-10wt%nickel-7.5wt%W-** wt%Co) Make the size of width-of-face [of 30mm] x length [of 50mm] x thick 3 mm, and it considers as a test piece base material. It is the MCrAlX alloy which has the composition shown in Table 2 at the one side by the low-pressure-plasma-spraying method 300 mum A under coat is formed in **. It is 30 micrometers in the same atmosphere about aluminum or an aluminum-8wt%Si alloy as an overcoat on it. What was constructed to ** was used as the thermal-spraying test piece. A high temperature corrosion test is a 90wt%Na2SO4-10wt%NaCl mixture medicine 1cm to the surface area of a test piece 2 They are 4hr(s) in the electric furnace which applied 25mg of hits and was held at 1000 degrees C after that. It was left and high-temperature-corrosion-proof nature was evaluated by measuring the penetration depth of a caustic agent component for the cross section of a sprayed coating with cutting and an optical microscope after that. In addition, the comparison examination prepared the thing of only a MCrAlX alloy sprayed coating, and performed the same high temperature corrosion test. Table 4 summarizes this result. Sprayed coating which does not prepare aluminum which is an overcoat, or an aluminum-8wt%Si alloy sprayed coating so that clearly from this result (No.5 -8) At the member of the example of comparison which it has, it is 28-70 micrometers. Although the internal invasion of the caustic agent to attain was accepted Member which has the sprayed coating which suits this invention (No.1 -4) It is 10-25 micrometers then. It remains in the range and it was checked that the internal invasion of a corrosion component is prevented by existence of aluminum sprayed coating.

[0043]
[Table 4]

No	皮膜の構成		高温腐食試験結果（μm）	備考
	MCrAlX合金溶射皮膜	オーバーコート溶射皮膜の有無	1080℃×1h後	
1	A	有*	10 ～ 20	発明例
2	B	有	12 ～ 25	
3	C	有	18 ～ 20	
4	D	有	15 ～ 20	
5	A	無	28 ～ 60	比較例
6	B	無	29 ～ 70	
7	C	無	35 ～ 65	
8	D	無	33 ～ 70	

（備考）(1) MCrAlX合金溶射皮膜厚は 300μm
(2) No.1のオーバーコートはAl-8wt%Si合金の溶射皮膜である。
(3) オーバーコートのAlあるいはAl合金溶射皮膜の厚さは30μm
(4) 高温腐食試験結果は最大侵食深さを示す（μm）

[0044] an example 4 -- in this example, the overcoat which is aluminum or aluminum alloy sprayed coating was formed on the MCrAlX alloy sprayed coating formed as a under coat, and the adhesion of a ceramic sprayed coating at the time of forming further the sprayed coating of the oxide system ceramics which consist of composition of 8wt%Y2O3-92wt%ZrO2 as topcoat on it was investigated As a test piece base material, it is the MCrAlX alloy thermal spray material shown in Table 2 as a under coat at this one side by the low-pressure-plasma-spraying method using nickel machine alloy used in the example 2 300 It formed in the thickness of mum and aluminum or the aluminum-3wt%Si alloy was further constructed as an overcoat on it at 30-micrometer **, respectively. Furthermore, what formed oxide system ceramics in the front face of these test pieces by the air plasma metal spray method as topcoat at the thickness of 300 micrometers was prepared. Thermal-shield coat made by the above methods (Thermal Barrier Coating) It experimented repeatedly until it made into 1 cycle operation which takes out outside a furnace, sprays the compressed air and test piece temperature cools to 150 ** and the oxide system ceramics of a test piece exfoliated, after heating for 30 minutes in the electric furnace held at 1150 degrees C. In addition, they are oxide system ceramics on a MCrAlX alloy sprayed coating without an overcoat as an example of comparison 300 What was constructed to mum ** was used.

[0045] Table 5 is what summarized these results, and is 300-350 at the coat (No.5-8) of the example of comparison. At the example of this invention (No.1-4), it is 400 altogether to ablation of oxide system ceramics having occurred by the time repeat. Bearing the repeat of heating-cooling more than a time was checked. This is aluminum 2O3 precise to aluminum sprayed coating in contact with oxide system ceramics. It generates and this is considered to have demonstrated an oxide system ceramic component and the outstanding unity.

[0046]

[Table 5]

No.	皮膜の構成			高温腐食試験結果（μm）	備考
	MCrAlX合金溶射皮膜	オーバーコート溶射皮膜	8YZ	1150℃×30min → 150℃	
1	A	有	有	405	発明例
2	B	有	有	450	
3	C	有*	有	480	
4	D	有	有	429	
5	A	無	有	318	比較例
6	B	無	有	300	
7	C	無	有	340	
8	D	無	有	350	

(備考) (1) MCrAlX合金の記号と化学成分は表2に示した通りである。
(2) No.3のオーバーコートはAl-3wt%Si合金の溶射皮膜である。

[0047]
[Effect of the Invention] As explained above, since this invention has formed aluminum or aluminum alloy sprayed coating in the atmosphere where it is the same on it, by the spraying process under the reduced pressure which does not contain oxygen substantially after aluminum content's forming a 2 - 18wt% MCrAlX alloy sprayed coating, while it is precise and excelling in adhesion with a base material, the member which shows good high-temperature-corrosion-proof nature can be offered. Moreover, this invention is excellent also in adhesion with the oxide system ceramic sprayed coating, under coat, and overcoat which are formed as topcoat. Therefore, after MCrAlX alloy sprayed coating formation, since treatment processes other than thermal spraying are omissible not to mention there being no degradation of the mechanical performance of the base material by operation of aluminum diffusion process as compared with the conventional method of performing aluminum diffusion process, shortening of sharp reduction of a manufacturing cost and production time is attained.

[Translation done.]